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Chemiluminescent reactions of group IV A atoms with PCI₅ and SnCl₄

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Earlier work on chemiluminescent (CL) reactions of group IV A atoms with halogens has been extended to two chlorine-rich molecules PCl_5 and $SnCl_4$. The CL products in these reactions were found to be group IV A dihalides formed in a one step mechanism instead of the two step mechanism proposed in the study of the reactions involving Br_2 , I_2 , and ICl. For PCl_5 , the CL products were found to be group IV A dichlorides, while for $SnCl_4$, the CL products are believed to be $SnCl_2$ for all three atoms. The overall absolute cross sections for the reactions have been estimated, as well as the relative cross sections as functions of collisional energy. The observation of different collisional energy dependence for the reactions of PCl_5 and $SnCl_4$, along with other evidence, suggests that two different mechanisms produce the CL products in the two groups of reactions.

I. INTRODUCTION

The chemiluminescent (CL) reactions of group IV A atoms with various halogens (F₂, Cl₂, Br₂, I₂, and ICl) have been studied extensively in both flame and flow experiments¹⁻⁵ and beam-gas experiments.⁶⁻⁹ Both group IV A monohalides and dihalides were observed. It is not surprising that the dihalides appear to be formed in a two step mechanism where vibrationally excited monohalides are formed in the first step, because addition of a halogen molecule in a single collision to form the group IV A dihalide is limited by radiative stabilization being much slower than dissociation. However, it is possible for a halogen-rich polyatomic molecule to provide two halogen atoms in a single step because the molecular fragment will be able to carry away the excess energy. Two such molecules were used in the present study, namely, PCl₅ and SnCl₄. A previous paper reported similar reactions of the same atoms with ClF₃, SF₄, and SF_6 to form the group IV A difluorides.⁸

CL products from the reactions of both PCl₅ and SnCl₄ with the ground states of Si, Ge, and Sn were observed. Spectral features of the emission from each of the reactions of PCl₅ and SnCl₄ with all the group IV A atoms are informative as to the identities of the emitters. It is proposed that the CL dihalides were MCl₂ (M = Si, Ge, and Sn) in the reactions of PCl₅, while the CL dihalides were all SnCl₂ in the reactions of SnCl₄ with all three atoms. That is, MCl₂ was formed in its ground electronic state and the molecular fragment SnCl₂ carries most of the excess energy in the form of electronic excitation.

The relative cross sections as functions of energy for all the reactions were obtained in time-of-flight (TOF) experiments. Distinctively different features for PCl₅ reactions and SnCl₄ reactions were found. The CL cross sections for SnCl₄ reactions increase with the collisional energy (E_c) , while for the most part, the CL cross sections for PCl₅ decrease with the increasing E_c . This difference further supports the proposal that the reactions proceed by different mechanisms.

Finally, the absolute cross sections for the CL reactions with PCl_5 and $SnCl_4$ were obtained by comparison with the CL reactions with F_2 and N_2O . It is noted that the reaction of Sn with PCl_5 has a particularly large CL cross section.

II. EXPERIMENT

The apparatus and the procedure used in this study has been described in detail previously.⁶⁻¹⁰

Briefly, the CL spectra were obtained in a molecular beam apparatus where the metals were vaporized in a high temperature effusive beam source. Typical source temperatures were 2000, 1850, and 1750 K for Si, Ge, and Sn, respectively. The group IV A vapors were collimated upon entering a seperately pumped chamber filled with PCl₅ or SnCl₄, whose pressures were typically about 10⁻⁴ Torr, as measured by a capacitance manometer. Chemiluminescence from the products was viewed at 90° to the beam through a 3/4 m Spex monochromator with a spectral bandpass of 3 nm followed by an RCA C31034 photomultiplier tube (PMT). The monochromator was controlled by a microcomputer and scanned to count the CL photons at different wavelengths in order to obtain the emission spectra, which were corrected later for spectral response using calibrated deuterium and quartz-halogen lamps.

To determine the effect on reactivity of exciting the group IV A atom to its metastable ${}^{1}D$ state, a dc discharge was employed in the Ge and Sn sources, as described previously.^{7,9}

The vapor of PCl_5 and $SnCl_4$ was introduced into the reaction chamber by heating a glass flask containing the chemicals which were used as provided by the supplier without further purification.

The TOF experiments measuring the collisional energy dependence of the CL reaction cross sections were carried out in a separate, but similar apparatus. The group IV A source temperatures were 2100, 1920, and 1840 K for Si, Ge, and Sn, respectively, which were slightly different from the other experiment. For the TOF experiments, a 13.3 cm di-

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ameter chopper wheel with six 1×10 mm equally distributed slots was rotated at 150 Hz, providing a beam open time of 26 μ s [full width at half-maximum (FWHM)]. The flight path in this apparatus from the wheel to the detection zone containing the gas reactants was 19.75 cm. Total chemiluminescence was collected directly by an EMI 9789B PMT without any interference filter. The photons were counted by a 100 channel multichannel analyzer (Honeywell SAI-42A) with a channel width of 5 μ s. The zero time was established by measuring light from the metal oven. Comparisons of the CL reaction cross sections with those for reactions with F₂ and N₂O were also carried out in this apparatus.

III. RESULTS AND DISCUSSION

Chemiluminescence from the products of the reactions of PCl_5 and $SnCl_4$ with all three atoms was observed. The UV-visible emission spectra which were recorded will be discussed first.

A. Emission spectra

The spectra from the reactions of unexcited Si, Ge, and Sn with $SnCl_4$ were very similar, as shown in Fig. 1. All three spectra peak at about 450 nm. The locations and breadth of



FIG. 1. Chemiluminescence spectra from the reactions of (a) Si; (b) Ge; and (c) Sn with $SnCl_4$. The peaks are assigned to emission of the ${}^{3}B_{1}$ state of SnCl₂ for all reactions.

the peaks indicate that the products are dichlorides.^{9,11-13} No major signal enhancements or spectral shifts were observed in using discharged beams of Ge and Sn, which contained substantial populations of the ¹D states of Ge and Sn. The signal dependence on SnCl₄ pressure showed that the reactions were all first order in SnCl₄. However, the identities of the CL products still cannot be ascertained since there are two possible CL dichloride products in a single collision between SnCl₄ and M (M = Si, Ge, and Sn):

$$\mathbf{M} + \mathbf{SnCl}_4 \rightarrow \begin{cases} \mathbf{MCl}_2^* + \mathbf{SnCl}_2 \\ \mathbf{MCl}_2 + \mathbf{SnCl}_2^* \end{cases}$$

In other words, either MCl_2 or $SnCl_2$ can be produced in an electronically excited state. Production of both products in electronically excited states, however, is energetically forbidden, as seen in Table I which gives estimates of the excergicities of the possible reactions.

It has been shown^{9,11-13} that the spectra from the ${}^{3}B_{1}-{}^{1}A_{1}$ emission of SiCl₂, GeCl₂, and SnCl₂ peak at 437, 441, and 449 nm, respectively. Since the current spectra from the three reactions peak at about 450 nm, the CL product is most likely SnCl^{*} rather than SiCl^{*} or GeCl^{*}. However, this conclusion is only tentative because of the small separation in wavelength of the peak emission of the three species. Fortunately, the reaction of Si and SnCl₄ provided further support for this proposal as to the identity of the products. In an earlier study⁹ of the reactions of Si with Cl₂ and ICl, as well as in the reaction with PCl₅ which will be discussed below, chemiluminescence from only the ${}^{1}B_{1}-{}^{1}A_{1}$ transition of SiCl₂ was observed. The absence of ${}^{3}B_{1} - {}^{1}A_{1}$ emission at longer wavelengths is believed to be caused by a much longer radiative lifetime of the ${}^{3}B_{1}$ state than the ${}^{1}B_{1}$ state, which would allow the ${}^{3}B_{1}$ state to exit the region viewed prior to radiating to the ${}^{1}A_{1}$ state. Therefore, the chemiluminescence in the region of the ${}^{3}B_{1} - {}^{1}A_{1}$ transition of the dichlorides in the reaction of Si with SnCl₄ is most sensibly assigned to excited SnCl₂ rather than SiCl₂. It is reasonable to assume that the reaction of Ge with SnCl₄ follows the same pattern of producing the ${}^{3}B_{1}$ state of SnCl₂. Although reactions of Ge with Cl₂, ICl, and PCl₅ do produce emission of the ${}^{3}B_{1}$ state of GeCl₂, its emission spectra peak at slightly shorter wavelengths than observed in the SnCl₄ reaction. For SnCl₄ reaction with Sn, there is no doubt, of course, that the CL product was SnCl₂. Hence, we have assigned the CL product from all three reactions to be SnCl₂. This assignment is consistent with the reaction energetics given in Table I, which also lists the maximum energies observed in the emission spectra. These energies are less than the total energies available to products, as expected because of some energy being possessed by the nonemitting products and the emitting ones after radiating.

For the reactions of PCl₅ with Si, Ge, and Sn, the spectra look quite different, especially in comparison of Si with the other two atoms, as shown in Fig. 2. The double peaked emission for Ge and Sn is assigned to ${}^{1}B_{1}-{}^{1}A_{1}$ and ${}^{3}B_{1}-{}^{1}A_{1}$ transitions of SnCl₂ and GeCl₂.^{9,11,12} However, in the case of Si + PCl₅, only the emission from the singlet state was observed, while the triplet was missing. Since there seems to

TABLE	I. Energetics o	f observed	reactions with	i probab	le emitting states.
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Reaction	$-\Delta H_0^0(kJ/mol)$	Emitting states	hv _{max} (kJ/mol)	
$\overline{\text{Si} + \text{SnCl}_4 \rightarrow \text{SiCl}_2 + \text{SnCl}_2}$	402 ^{a,b}	$\operatorname{SnCl}_2({}^3B_1)$	315	
$Ge + SnCl_4 \rightarrow GeCl_2 + SnCl_2$	360 ^{b,c}	$\operatorname{SnCl}_{2}({}^{3}B_{1})$	297	
$Sn + SnCl_4 \rightarrow SnCl_2 + SnCl_2$	351 ^b	$\operatorname{SnCl}_{2}({}^{3}B_{1})$	298	
$Si + PCl_3 \rightarrow SiCl_2 + PCl_3$	540ª	$SiCl_2(^1B_1)$	411	
$Ge + PCl_3 \rightarrow GeCl_2 + PCl_3$	494 ^{a,c}	GeCl ₂ (${}^{1}B_{1}, {}^{3}B_{1}$)	403	
$Sn + PCl_{s} \rightarrow SnCl_{2} + PCl_{3}$	485 ^{a,b}	$SnCl_{2}(^{1}B_{1}, ^{3}B_{1})$	376	

* Reference 14.

^bReference 15.

[°]Reference 11.

be no reason why formation of the triplet state should be forbidden,⁹ the absence of ${}^{3}B_{1} - {}^{1}A_{1}$ emission in the spectrum is most likely caused by a long radiative lifetime of the ${}^{3}B_{1}$ state. The smaller spin-orbit interaction in SiCl₂ compared to the Ge and Sn dichlorides is undoubtedly responsible for a longer radiative lifetime. As for the SnCl₄ reactions, the maximum energies observed in emission from the PCl₅ reactions are consistent with the proposed mechanisms and energetics^{11,14,15} shown in Table I.



FIG. 2. Chemiluminescence spectra from the reactions of (a) Si; (b) Ge; and (c) Sn with PCl₅. For the reaction of Si, the peak is assigned to emission of SiCl₂ (¹B₁), and for the reactions of M = Ge and Sn, the peaks are assigned from shorter wavelength to emission of ¹B₁ and ³B₁ states of MCl₂.

The CL signal dependence on the PCl_5 pressure established that these were first order reactions in PCl_5 . This contrasts with reactions with halogen molecules to form dihalides, which require a secondary collision of a monohalide intermediate, making the overall process second order in halogen.

Although in reactions of both $SnCl_4$ and PCl_5 the CL product was produced in a single collision and was a dichloride, the mechanisms are quite different. For PCl_5 , the group IV A atoms abstract two Cl atoms from PCl_5 to form the CL product MCl_2^* , whereas in the case of $SnCl_4$, the group IV A atoms carry away two Cl atoms, leaving the molecular fragment $SnCl_2$ in an excited state.

In order to understand the two reactions further, we studied them in a TOF apparatus to obtain the collisional energy dependence of the CL reactions.

B. TOF study and CL cross sections

The TOF spectra were taken without wavelength selection and were integrated to obtain the relative CL cross sections for comparison with other reactions for which absolute CL cross sections had been determined previously. For the CL reactions of Sn with PCl₅ and of Ge with SnCl₄, comparisons of wavelength resolved spectra were made with CL reactions with F_2 . If the electronically excited group IV A dichlorides radiate more slowly than the time it takes them to traverse the region viewed (10-100 μ s), then the absolute cross sections found will be lower bounds on the true ones.¹⁶ A determination using laser-induced fluorescence in our laboratory of a radiative lifetime of 14 μ s for SnCl₂ (³B₁) indicates that, at least in that case, most of the emitting species were observable. The results for the rates of the CL reactions relative to N_2O and F_2 CL reaction rates are shown in Table II. These relative rates are based on the assumption that radiation is complete for all of the observed products. Incomplete radiation may be responsible for the smaller rates found in the reactions of Si and Ge with PCl₅ compared to the reaction of Sn with PCl₅, which gave bright chemiluminescence that was clearly visible even with PCl, pressures as low as 10⁻⁴ Torr. Absolute cross section estimates based on absolute values found earlier for the F₂ CL reactions⁶ are given in Table II. Their uncertainties are at least as large as the 50% uncertainties associated with F_2 cross sections. Estimates for absolute cross sections can also be made for the

TABLE II. Relative rate constants and absolute cross section for the CL reactions.

Reaction	$T_{\rm eff}({f K})^{ m a}$	$k/k(N_2O)$	$k/k(\mathbf{F}_2)$	$\sigma(\text{\AA}^2)^{b}$
$\overline{\text{Si} + \text{SnCl}_4 \rightarrow \text{SiCl}_2 + \text{SnCl}_2^*}$	1920		0.60	0.63
$Ge + SnCl_4 \rightarrow GeCl_2 + SnCl_2^*$	1570	21	0.053	0.19
$Sn + SnCl_4 \rightarrow SnCl_2 + SnCl_2^*$	1360	5.7	0.026	0.08 (0.038)
$Si + PCl_5 \rightarrow SiCl_2^* + PCl_3$	1890	4.3	0.24	0.38
$Ge + PCl_5 \rightarrow GeCl_2^* + PCl_3$	1500	107	0.28	0.98
$Sn + PCl_5 \rightarrow SnCl_2^* + PCl_3$	1280	347	1.59	4.9 (2.3)

^a Effective translational temperatures for beam-gas reactions.

^bAbsolute cross sections based on F_2 CL rates, except for the values within parentheses, which are based on N₂O CL rates.

Sn reactions by comparison with the absolute rate constant for Sn + N₂O \rightarrow SnO + N₂ given by Felder and Fontijn^{17,18} of (8.9 ± 4.0) × 10⁻¹³ exp[- (2260 ± 180)/T] cm³ s⁻¹ with T = 1840 K,¹⁹ and a low pressure quantum yield of 0.15 ± 0.09. The values obtained for the cross sections shown in parentheses are in acceptable agreement with the F₂ based results in light of the large uncertainties.

From the original TOF spectra, the velocity dependence and, therefore, the collisional energy dependence of the cross sections of these CL reactions can be obtained.¹⁰ The parameters E_0 and n in an assumed form for the cross sections proposed by Gonzales-Ureña²⁰

$$\sigma(E_c) \propto (E_c - E_0)^n / E_c$$

were varied in order to fit the observed TOF spectra and Table III gives the values obtained. Figure 3 shows the fits obtained for the TOF spectra when this form for the cross section is convoluted with the velocity distributions of the scattering gases and the atoms for the two Si reactions. Only data points with intensity greater than 20% of the maxima were used in the fitting procedure. Figures 4 and 5 show the relative CL cross sections as functions of collisional energy (E_c) for reactions with SnCl₄ and PCl₅, respectively. The different pattern of these curves is apparent. For $SnCl_4$, the cross sections of the CL reactions increase with E_c in the collisional energy range used in this study, suggesting the presence of barriers in the entrance channel that can be overcome by increasing E_c . Barriers associated with other parts of the potential energy surfaces are less likely to be overcome by increasing E_c . For PCl₅, on the other hand, the CL cross sections drop rapidly with increasing E_c after a low-energy

TAB	LE III.	Energy	dependence	parameters for	or the	CL reactions.
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Reaction	E_0 (kJ/mol)	n
$\frac{1}{\text{Si} + \text{SnCl}_4 \rightarrow \text{SiCl}_2 + \text{SnCl}_2^*}$	0.0	1.25
$Ge + SnCl_4 \rightarrow GeCl_2 + SnCl_2^*$	13.0	0.83
$Sn + SnCl_4 \rightarrow SnCl_2 + SnCl_2^*$	12.9	2.03
$Si + PCl_s \rightarrow SiCl_s^* + PCl_s$	10.0	0.34
$Ge + PCl_{2} \rightarrow GeCl_{2}^{*} + PCl_{3}$	5.0	0.29
$Sn + PCl_{3} \rightarrow SnCl_{2}^{*} + PCl_{3}$	6.4	0.24

maximum. This suggests that when M reacts with PCl_5 to form MCl_2 and PCl_3 , a relatively long-lived intermediate is involved. One can speculate that when M collides with PCl_5 at high velocity, it is more likely to abstract one rather than two Cl atoms and to leave quickly without having a chance to form MCl_2^* . MCl could be a major product which was undetectable in our experiments because it is limited for energetic reasons to its ground electronic state. When M approaches PCl_5 slowly, it has more time after the first Cl atom abstraction in which to encounter a second Cl atom and to produce MCl_2^* . The involvement of a long-lived intermediate can also explain the violation of spin conservation which



FIG. 3. TOF spectra for CL reactions of Si with (a) SnCl₄ and (b) PCl₅. Solid curves represent the calculated fits to the experimental points having values greater than 20% of the maximum.

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FIG. 4. Relative CL cross sections as functions of collision energy for $M + SnCl_4$. Starting from the top, M = Si, Ge, and Sn.

occurs when MCl₂ is formed in the ${}^{1}B_{1}$ state from reaction of a triplet atom with a singlet molecule. The longer life might allow repeated crossings of the region of singlet-triplet surface intersections and hence transfer to a triplet surface. Notably, reaction with SnCl₄ does not violate spin conservation since no MCl₂ in the ${}^{1}B_{1}$ state is observed, even though its formation would be exothermic in the case of M = Si and close to thermoneutral for M = Ge and Sn. This is consistent with the direct character of the reaction inferred from the collisional energy dependence. Another indication that a singlet potential energy surface was not involved in the SnCl₄ reactions came from the absence of changes in chemiluminescence brought about by adding ^{1}D states of Ge or Sn. Adiabatic orbital correlations can be used to explain the direct reaction of M (³P) with SnCl₄ to form SnCl₂ in the ³B₁ state and MCl_2 in the ground ${}^{1}A_1$ state. The electrons which are freed when the two Sn-Cl bonds are broken have maximum density in a plane perpendicular to the plane of the $SnCl_2$ product. This associates them with $5p_z$ and $5p_x$ orbitals on Sn (with axes definitions given by Herzberg²¹), leading to an overall ${}^{3}B_{1}$ symmetry. The newly formed MCl₂ is expected to be in the ${}^{1}A_{1}$ state since the unpaired p electrons on M go into the M-Cl bonds and the remaining valence electrons on M are paired.



FIG. 5. Relative CL cross sections as functions of collision energy for $M + PCl_5$. Starting from the top, M = Si, Ge, and Sn.

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¹⁹ The temperature in this rate constant expression was taken to be that of the Sn source rather than the effective translational temperature, since the temperature dependence is thought to arise from the need to populate the ${}^{3}P_{1}$ state of Sn (Ref. 17).

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